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TITLE: THE USE OF MARKERS TO ELUCIDATE REACTING SPUTTERING PROCESSES

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The Use of Markers to Elucidate Reactive Sputtering Processes

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The mechanism of reactive sputtering is very complex due to the nature of the plasma and the many excited ion states that are created. This allows the possibility that compounds are formed in the glow, on the target and at the substrate. It is very difficult to separate these sources during operation, and as a result, most information on the topic remains empirical. This experiment attempts to separate the plasma/substrate effects from the target effect. The reactive gases of nitrogen, ammonia, carbon monoxide and methane were introduced to a steady state deposition of aluminum using a planar magnetron operating at ~ 400 volts. As soon as the plasma was found to change color, the deposition was terminated and the gases pumped out. A marker of copper was deposited on the substrate. Argon was re-introduced to the chamber and sputtering continued. In this fashion, the effect of the compound formed at the target was separated from the plasma/substrate effects.

The resulting films were analyzed by Auger Depth Profiling. The location and intensity of the nitrogen and carbon signals give clues to the nature of the compound origins. A significant portion of the

observed compound comes from the target. This result is interpreted in terms of low energy ion implantation in the target. Theoretical Monte Carlo calculations for ion ranges in solids are used to support a model to describe these findings. The individual differences in the results between ammonia and methane are explored in terms of the different behavior of the plasma target interaction during gas introduction rather than on a chemical reactivity basis. A connection between cathode fall voltage and target physics is proposed in terms of the ion ranges in the target and the efficiency of compound production.

INTRODUCTION

Reactive sputtering is a tool that has been widely used for many years to produce all types of compound coatings.[1] By varying the mixtures of the gases in the chamber during deposition, the desired properties can usually be obtained. This work attempts to locate the source of the compound formation, whether it is formed on the target, in the glow, or on the substrate. Without lengthy arguments, a simple experiment can be performed which will attempt to decouple the target effect from the glow/substrate interaction. Work done by Kabalian[2] et al has shown that the threshold for compound formation can be quite low for nitrogen in aluminum, so that it is possible for the compound to be formed at any of the regions mentioned.

The way in which the target may be decoupled is to consider the low energy ion implantation of the reactive species into the target. The plasma potential can be on the order of 30 eV, thus allowing the

remaining voltage, the cathode fall voltage, to be available for the bombarding ions. If the target voltage is ~ 400 volts, then the cathode fall voltage is on this order of magnitude. Low energy ion implantation simulation studies show that nitrogen and carbon can penetrate 0.5 to 3.5 nm. If the sputter rate is not too high, it is possible to introduce the reactive gas and quench the plasma before enough of the target material is eroded to cause significant deposit to arrive at the substrate. If a fiduciary marker is deposited on the substrate at this time, then the sputtering resumed in argon only, the remaining compound in the target will appear on the trailing side of the marker.

THEORY

Reactive sputter deposition has been a subject of interest for some time. The compounds that are observed at the substrate could be formed at the target, in the glow, or at the substrate. The problem with the formation of the compound in the glow is the conservation of momentum and energy requires a many body interaction which is not likely in the typical operating pressures of most sputter apparatus. The bulk of the early work has favored the substrate as the likely candidate for synthesis.[1] However, the species from the target are not very energetic when they arrive at the substrate due to the gas collisions. Studies of the ions produced in the glow are subject to the selection rules for ion production. Similarly, excited states that give rise to the atomic emission can be deceptive in determining the nature of the species arriving from the target. This treatment does not attempt to claim that all the compound comes from the target, but a significant fraction of

the compound is thought to originate at the target. The majority of the energy available for compound formation is available at the target due to the cathode fall voltage. This voltage is significant enough to produce several layers of the compound due to the low energy ion implan-tation. The remaining problem is the sputtering of the compound without dissociation. This is a se arate question in itself, and will not be addressed here. However, it is clear that if the target surface is not fully covered by compound, then free metal is almost certainly to be sputtered.

More recently, a number of authors have indicated that a target not fully covered by compound does lead to films that are sub-stoichiometric. Maniv and Westwood[3,4] found that films of Al_2O_3 were incompletely oxidized if the oxygen partial pressure was insufficient to completely oxidize the target. R. B. Van Dover[5] et.al. found an increase in the Tc of NbN films if the sputter rate was not matched with the nitriding of the target. Affinito and Parsons[5] report a method of varying the composition of films based on the discharge characteristics. They find that films of AlN are fully stoichiometric at high partial pressures of N_2. They measure the light emission from the free excited aluminum and find that it drops to zero when good films are prepared. However, they do not see any emission lines due to AlN, and conclude that none is in the glow. Arita and Gaskat[7] find that Al sputtered in mixtures of N_2/Ar becomes more AlN as the nitrogen content is increased to a certain point, above which no further changes in the growth rate are observed. They indicate that a flux of Al and AlN is most likely produced with the free aluminum at the substrate adsorbing nitrogen to give full

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stoichiometry. Other work by Aita and Myers[8] on the deposition of TaN

using Glow Discharge Mass Spectrometry (GDMS) find a significant frac-

tion of TaN+ in addition to Ta+ arriving at the substrate. The

substrate bias appears to change the ratio of Ta+ to TaN+, but the trend

is toward an increasing amount of observed TaN+ with increasing partial

pressure of N_2. Other GDMS results on copper oxides by Purdes et.al.[9]

and Tantalum oxides by Bolker[10] et.al. find that the free Ta+ signals

become very small when good Ta_2O_3 films are being deposited.

These experimental observations appear to point toward the target

physics as being significant in the production of good compound

material. The computations[11] using the low energy ion implentation

simulations, indicate that the usual voltages present in the glow can

place nitrogen or carbon at depths ~ 1-2 nm. These ranges are in

agreement with other observations that the target surface is covered

with compound. Using a fiduciary of copper, the material can be subse-

quently sputtered, collected on the substrate and subsequently analyzed

by Auger Electron Spectroscopy and Depth Profiling techniques. The use

of the GDMS technique is quite powerful and has shown a demonstrated

success in the production of good material but can still be limited by

the measurement of only the excited species which is a small fraction of

the total flux. The sputter profile method has the potential of examin-

ing the complete history of the interactions.

EXPERIMENT

Four different gases were used to check the energy partitioning of

the molecules, and to vary slightly the atomic number. These gases, N_2,

NH_3, CO, and CH_4 were chosen because o. their low chemisorption on atomically clean aluminum surfaces.[12] An orbitor magnetron was used as the sputter source. The typical argon pressure during operation was ~ 0.7 Pa. Aluminum was deposited to a thickness of ~ 150 nm and then a pulse of gas was introduced for a period of 0.25-2 seconds. At the end of this period, the gas and the power supply were simultaneously cut off. The vacuum system was then purged of the argon/reactive gas, and a marker of copper was deposited on the substrate to a thickness of ~ 70 nm. The system was filled with argon, and sputtering resumed. This set of conditions was repeated for three total cycles in each experiment. The reactivity of each gas was also checked by introducing a particular species without the sputter discharge operating. In each case, there was no evidence of the nitrogen or carbon species found in the films on either side of the marker. Thus, it is reasonably certain that any of the elements measured by Auger Depth Profiling are due to the plasma or target effects.

The details of the source and power supply characteristics also play a crucial role in this experiment. The power supply has an internal resistance of ~ 300 ohms. This implies that any change in the operating current during the gas pulsing can increase or decrease the sputter voltage due to a change in the glow impedance caused by the differences in the secondary electron yield from compound formation. Secondly, the current density must be known. The total discharge current was ~ 2 amperes. The area of the target covered by the glow was ~ 176 cm^2. Thus, the current density before the test gas was pulsed into the chamber was ~ 11 ma/cm^2. These conditions, combined with the

position of the substrate gave a deposition rate of ∿ 2 nm/sec. In the case of the CO and CH_4, the operating voltage of the power supply, and, therefore, the plasma conditions remain essentially constant. The nitrogen introduction causes the power supply to drop to ∿ 275 volts, and the ammonia causes the power supply to drop to ∿ 200 volts. Thus, the energy per atom must be computed based on the observed voltage.

After each deposition was completed, the samples were introduced to an ultra high vacuum chamber where Auger depth profiling could be accomplished. The samples were profiled using a ∿ 1.5 keV argon beam, with ∿ 0.5 uA of electron beam current at 5 keV.

RESULTS AND DISCUSSION

A Monte Carlo simulation[11] was used to describe the low energy ion implantation. The results of this computation for various gases and substrate materials has been found to be in reasonable experimental agreement with implant voltages of 0.5 to 5 keV. Assuming that this treatment is valid to the lower energies encountered in this experiment, the theoretical depth distributions are shown in Figs. 1a to 4a. The depth distributions are computed with a 0.1 nm resolution, which is clearly unphysical, but was used to produce a smooth computation. In reality, the atoms may come to rest in some more discrete set of locations in the target. Figures 1a and 2a show the profiles for the carbon monoxide and methane. The carbon monoxide profile peaks between ∿ 0.7 and ∿ 1.7 nm. The methane profile peaks between ∿ 1 and 2.7 nm.

Thus, as the sputtering process continues during the implantation process, some of the surface will be removed during the gas introduction. If there are $\sim 2.5 \times 10{+}15$ atoms per layer, and assuming a current density of 11 ma, and a sputter yield of ~ 0.4 atoms per argon atom, the etch rate of the target is ~ 13 layers/sec or about 5.4 nm/sec. It is clear that during the doping process, the surface is being eroded away at depths in excess of the implant depth. Thus, it is impossible to dope the target without some of the compound being sputtered to the substrate, unless very short exposure times are used. Since detectability depends on the total current, i.e. dose, a compromise must be made. As a result, several experiments were performed with each gas using the introduction times of 0.5, 1 and 2 seconds. As the times are increased, the amount of carbon/nitrogen on the substrate/glow side should increase with changes on the target side reflecting the depth/dose character.

The substrate will act as an integrator for all the effects, and essentially is a time record for the various possibilities of compound formation. The target can only reach a steady state condition between implant dose, range, and erosion rates. This phenomena can be thought of as an altered layer. Other parameters such as the sputter yield for the individual compounds can also alter the results. However, examination of Figs. 1b-1d and 2b-2d show the results of the carbon profiles for the carbon monoxide and the methane. The amount of carbon on the substrate/glow side for the carbon monoxide is higher than on the target side. This is consistent with the shallow doping of the target

versus the erosion rate. The methane, however, is exactly reversed. The amount of carbon from the target side is always greater than on the substrate side for these experiments. This result is consistent with an implant depth that is ∿ twice the range from the carbon monoxide.

The nitrogen and ammonia experiments give essentially the same results. This is due to the fact that the power supply voltage is lower for the ammonia than for the nitrogen. After partitioning the energy to the various components, the kinetic energy per nitrogen is essentially the same. Thus, the range of the nitrogen in the target should be the same for both of the nitrogens. The range calculations for the nitrogen and ammonia are shown in Figs. 3a and 4a. The results of the depth profiles are shown in Figs. 3b-3d and 4b-4d.

The results of these experiments are consistent with a picture of reactive sputtering that produces the compound in the target which is subsequently sputter deposited to the substrate.

CONCLUSIONS

The marker experiments do show a decoupling of the target and plasma/substrate interaction within the spatter etch rate and doping time constraints. The data does show clear evidence for the deposition of compound from the target which is thought to be due to the near surface modification from the cathode fall voltage. The energy partitioning of the carbon in either carbon monoxide or methane yields the expected results, namely that the deeper the implant, the greater the

portion of carbon from the target. The nitrogen and ammonia results were similar in nature due to the reduced voltage from the sputter power supply. The results are still consistent with the target being doped, in that the nitrogen ranges in the target are essentially identical.

In conclusion, this experiment does not prove that all the compound is formed and sputtered from the target, but does indicate that a significant fraction is formed and sputtered from the target. The data from this experiment is consistent with a model which indicates that the reactive species is implanted in the target, subsequently eroded away and contributes to the observed compound films.

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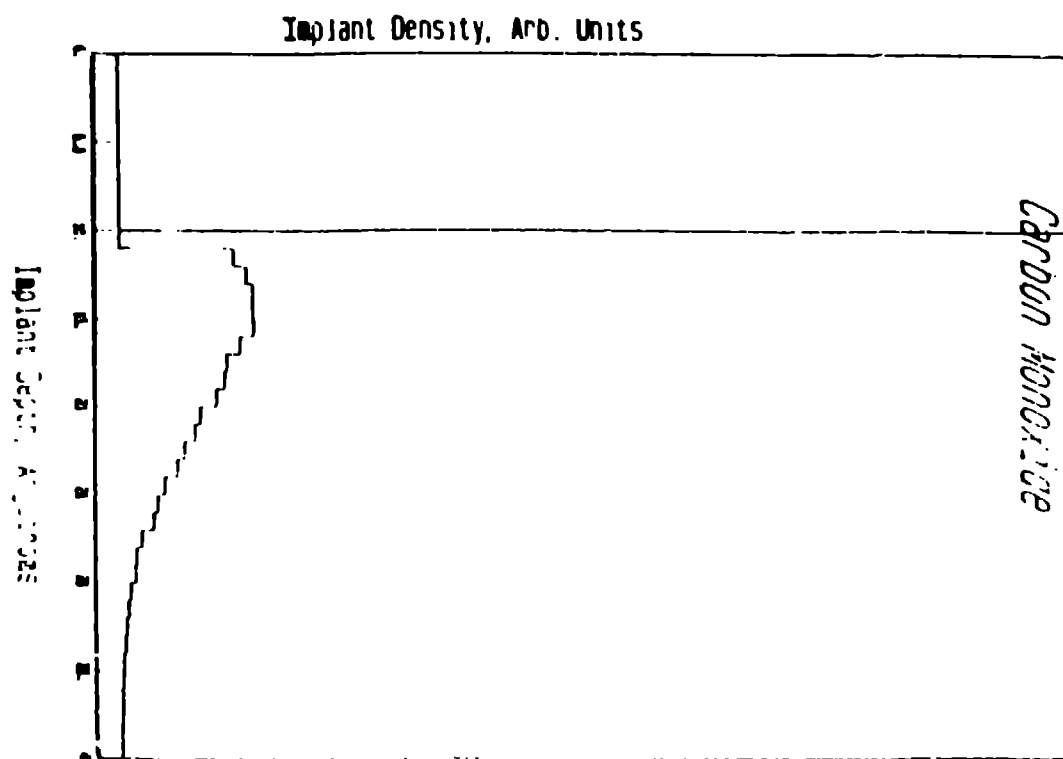
Figure 1. The ion range distribution for carbon monoxide is shown. It is assumed that the molecules dissociate on impact with the substrate, and each atom proceeds on its own. The fraction of the energy given to the carbon atom is (12/28) 0.42 or ~ 160 volts. The surface peak is obtained through the use of a surface trap. As low energy ions attempt to escape into the vacuum, they can be effected by such forces as bonding, van der Waals, or work function effects. Figures b-d show the typical depth profiles for the carbon on the substrate and target side as a function of dose.

Figure 2. The methane range distribution is shown with the depth profiles in b-d. The mass partition of the energy gives ~ 286 volts to the carbon atom. The range for the carbon is ~ twice the range due to the CO molecule. Thus, it is possible to dose the target and stop before significant sputtering occurs. This is reflected in a larger carbon signal on the target side than on the glow/substrate side.

Figure 3. Computed range distribution for nitrogen on the aluminum target is shown. The cathode voltage falls to ~ 275 volts, leaving ~ 140 volts per atom. The range is similar to the carbon from the CO molecule. The depth profiles have the same type of behavior as the shallow implant. There is some compound that is observed from the target.

Figure 4. The ammonia profile is computed based on the reduced cathode fall voltage of 200 volts. The mass partition to the nitrogen (14/17) to 0.82 gives ~ 165 volts to the nitrogen. This energy is similar to the nitrogen, and gives similar profile results shown in b-1.

Implant Density, Arb. Units

Carbon Monoxide

Implant Depth, A

Num. Peak to Peak Amp.   Num. Peak to Peak Amp.   Num. Peak to Peak Amp.

Be-Ion Dept.   Be-Ion Dept.   Be-Ion Dept.

Al
C
O

Implant Density, Arb. Units

Methane

Implant Depth, Angstroms

Norm. Peak to Peak Amp

Norm. Peak to Peak Amp

Norm. Peak to Peak Amp

Sputter Depth

Sputter Depth

Sputter Depth

2 sec

.5 sec

.5 sec

A

C

C

Implant Density, Arb. Units

Implant Depth, Angstroms

Nitrogen

Noise Peak to Peak Amp   Noise Peak to Peak Amp   Noise Peak to Peak Amp

Sputter Depth   Sputter Depth   Sputter Depth

N

C

Al